

PATENT COOPERATION TREATY

From the
INTERNATIONAL SEARCHING AUTHORITY

PCT

WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY

(PCT Rule 43bis.1)

To: Peter Ganjian
3146 North Verdugo Road
Glendale, CA 91208-1665

Date of mailing
(day/month/year) 24 JUL 2007

Applicant's or agent's file reference
MARGAR1.1PCT

FOR FURTHER ACTION

See paragraph 2 below

International application No.
PCT/US 06/26169

International filing date (day/month/year)
03 July 2006 (03.07.2006)

Priority date (day/month/year)
05 July 2005 (05.07.2005)

International Patent Classification (IPC) or both national classification and IPC
IPC(8) - C03C 3/247, C03C 3/16, C03B 25/00 (2007.01)
USPC - 501/44, 501/45, 65/117

Applicant MARGARYAN, Alfred A.

1. This opinion contains indications relating to the following items:

- ☒ Box No. I Basis of the opinion
- ☐ Box No. II Priority
- ☐ Box No. III Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- ☐ Box No. IV Lack of unity of invention
- ☒ Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- ☐ Box No. VI Certain documents cited
- ☐ Box No. VII Certain defects in the international application
- ☐ Box No. VIII Certain observations on the international application

2. FURTHER ACTION

If a demand for international preliminary examination is made, this opinion will be considered to be a written opinion of the International Preliminary Examining Authority ("IPEA") except that this does not apply where the applicant chooses an Authority other than this one to be the IPEA and the chosen IPEA has notified the International Bureau under Rule 66.1bis(b) that written opinions of this International Searching Authority will not be so considered.

If this opinion is, as provided above, considered to be a written opinion of the IPEA, the applicant is invited to submit to the IPEA a written reply together, where appropriate, with amendments, before the expiration of 3 months from the date of mailing of Form PCT/ISA/220 or before the expiration of 22 months from the priority date, whichever expires later.

For further options, see Form PCT/ISA/220.

3. For further details, see notes to Form PCT/ISA/220.

Name and mailing address of the ISA/US
Mail Stop PCT, Attn: ISA/US
Commissioner for Patents
P.O. Box 1450, Alexandria, Virginia 22313-1450
Facsimile No. 571-273-3201

Date of completion of this opinion
07 February 2007 (07.02.2007)

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
PCT OSP: 571-272-7774

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 06/26169

Box No. I Basis of this opinion

1. With regard to the **language**, this opinion has been established on the basis of:
☒ the international application in the language in which it was filed
☐ a translation of the international application into _____, which is the language of a translation furnished for the purposes of international search (Rules 12.3(a) and 23.1(b)).
2. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application and necessary to the claimed invention, this opinion has been established on the basis of:
 - a. type of material
☐ a sequence listing
☐ table(s) related to the sequence listing
 - b. format of material
☐ on paper
☐ in electronic form
 - c. time of filing/furnishing
☐ contained in the international application as filed
☐ filed together with the international application in electronic form
☐ furnished subsequently to this Authority for the purposes of search
3. ☐ In addition, in the case that more than one version or copy of a sequence listing and/or table(s) relating thereto has been filed or furnished, the required statements that the information in the subsequent or additional copies is identical to that in the application as filed or does not go beyond the application as filed, as appropriate, were furnished.
4. Additional comments:

**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 06/26169

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	<u>1-14</u>	YES
	Claims	<u>NONE</u>	NO
Inventive step (IS)	Claims	<u>1-14</u>	YES
	Claims	<u>NONE</u>	NO
Industrial applicability (IA)	Claims	<u>1-14</u>	YES
	Claims	<u>NONE</u>	NO

2. Citations and explanations:

Claims 1-14 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest the combination of aluminum phosphate, barium phosphate and bismuth phosphate in a doped glass composition in the claimed amounts. Conventional fluorophosphate glasses do not contain bismuth phosphate. Typically such glasses comprise bismuth oxide rather than bismuth phosphate as taught in US 3,281,254 A to Weidel.

US 6,495,481 B1 (Margaryan) and Fluorophosphate Vitreous Systems by Margaryan teach the use of various metaphosphates including aluminum metaphosphate and barium metaphosphate, but do not teach bismuth metaphosphate. Margaryan teaches barium fluoride as well as fluorides containing Ca, Mg, Pb and Bi. Further Margaryan teaches rare earth dopants including M₂O₃ and MF₃ where M is selected from the Lanthanide series. However, Margaryan does not teach or fairly suggest a composition of aluminum metaphosphate, barium metaphosphate, and bismuth metaphosphate with barium fluoride, and with one of CaF₂, MgF₂, PbF₂, or BiF₂ and further with a Lanthanide series oxide or fluoride as a dopant. The specific mol basis percent composition claimed is also not taught or fairly suggested by Margaryan.

US 5,858,465 A to Hunt et al. (hereinafter "Hunt") teaches aluminum metaphosphate, Barium metaphosphate and Bismuth phosphate, but not Bismuth metaphosphate. In addition Hunt does not teach production of a bismuth fluorophosphate glass, but teaches combustion chemical vapor deposition (CCVD) of phosphate coatings on a substrate. Further, Hunt does not teach fluorides except to teach that CCVD can be used to deposit coatings of oxides, nitrides, carbides, fluorides, borides, and some elements. Further Hunt does not teach a rare earth dopant of the formula M₂O₃ or MF₃ where M is selected from the Lanthanide series. Hunt does not teach percent composition of the various components, but teaches deposition of single species phosphate films.

Claims 1-14 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY (Chapter I of the Patent Cooperation Treaty)

(PCT Rule 44*bis*)

Applicant's or agent's file reference MARGAR1.1PCT	FOR FURTHER ACTION	See item 4 below
International application No. PCT/US2006/026169	International filing date (<i>day/month/year</i>) 03 July 2006 (03.07.2006)	Priority date (<i>day/month/year</i>) 05 July 2005 (05.07.2005)
International Patent Classification (8th edition unless older edition indicated) See relevant information in Form PCT/ISA/237		
Applicant MARGARYAN, Alfred, A.		

1.	This international preliminary report on patentability (Chapter I) is issued by the International Bureau on behalf of the International Searching Authority under Rule 44 <i>bis</i> .1(a).																								
2.	This REPORT consists of a total of 4 sheets, including this cover sheet. In the attached sheets, any reference to the written opinion of the International Searching Authority should be read as a reference to the international preliminary report on patentability (Chapter I) instead.																								
3.	<p>This report contains indications relating to the following items:</p> <table style="width: 100%;"> <tr> <td style="width: 10%; text-align: center;"><input checked="" type="checkbox"/></td> <td style="width: 30%;">Box No. I</td> <td style="width: 60%;">Basis of the report</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. II</td> <td>Priority</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. III</td> <td>Non-establishment of opinion with regard to novelty, inventive step and industrial applicability</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. IV</td> <td>Lack of unity of invention</td> </tr> <tr> <td style="text-align: center;"><input checked="" type="checkbox"/></td> <td>Box No. V</td> <td>Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. VI</td> <td>Certain documents cited</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. VII</td> <td>Certain defects in the international application</td> </tr> <tr> <td style="text-align: center;"><input type="checkbox"/></td> <td>Box No. VIII</td> <td>Certain observations on the international application</td> </tr> </table>	<input checked="" type="checkbox"/>	Box No. I	Basis of the report	<input type="checkbox"/>	Box No. II	Priority	<input type="checkbox"/>	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability	<input type="checkbox"/>	Box No. IV	Lack of unity of invention	<input checked="" type="checkbox"/>	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement	<input type="checkbox"/>	Box No. VI	Certain documents cited	<input type="checkbox"/>	Box No. VII	Certain defects in the international application	<input type="checkbox"/>	Box No. VIII	Certain observations on the international application
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4.	The International Bureau will communicate this report to designated Offices in accordance with Rules 44 <i>bis</i> .3(c) and 93 <i>bis</i> .1 but not, except where the applicant makes an express request under Article 23(2), before the expiration of 30 months from the priority date (Rule 44 <i>bis</i> .2).																								

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No. +41 22 338 82 70	<table border="1" style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 50%;">Date of issuance of this report 09 January 2008 (09.01.2008)</td> <td style="width: 50%;">Authorized officer</td> </tr> <tr> <td colspan="2" style="text-align: center; padding: 10px;"> <div style="font-size: 1.2em; font-weight: bold;">Nora Lindner</div> </td> </tr> <tr> <td colspan="2">e-mail: pt02.pct@wipo.int</td> </tr> </table>	Date of issuance of this report 09 January 2008 (09.01.2008)	Authorized officer	<div style="font-size: 1.2em; font-weight: bold;">Nora Lindner</div>		e-mail: pt02.pct@wipo.int	
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(day/month/year) 24 JUL 2007

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FOR FURTHER ACTION

See paragraph 2 below

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For further options, see Form PCT/ISA/220.

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P.O. Box 1450, Alexandria, Virginia 22313-1450
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Lee W. Young

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a. type of material

- ☐ a sequence listing
☐ table(s) related to the sequence listing

b. format of material

- ☐ on paper
☐ in electronic form

c. time of filing/furnishing

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**WRITTEN OPINION OF THE
INTERNATIONAL SEARCHING AUTHORITY**

International application No.

PCT/US 06/26169

Box No. V Reasoned statement under Rule 43bis.1(a)(i) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims	1-14	YES
	Claims	NONE	NO
Inventive step (IS)	Claims	1-14	YES
	Claims	NONE	NO
Industrial applicability (IA)	Claims	1-14	YES
	Claims	NONE	NO

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Claims 1-14 have industrial applicability as defined by PCT Article 33(4) because the subject matter can be made or used in industry.

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
11 January 2007 (11.01.2007)

PCT

(10) International Publication Number
WO 2007/005953 A2

(51) International Patent Classification:

C03C 3/16 (2006.01) **C03B 11/08** (2006.01)
C03B 3/02 (2006.01) **C03B 25/00** (2006.01)

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PCT/US2006/026169

(22) International Filing Date: 3 July 2006 (03.07.2006)

(25) Filing Language: English

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(30) Priority Data:

11/174,862 5 July 2005 (05.07.2005) US

(71) Applicants and

(72) Inventors: **MARGARYAN, Alfred, A.** [US/US]; 370 W. PIONEER DRIVE, Apt. #107, Glendale, CA 91203 (US).
MARGARYAN, Ashot, A. [US/US]; 370 W. PIONEER DRIVE, Apt. #206, Glendale, CA 91203 (US).

(74) Agent: **GANJIAN, Peter**; 3146 North Verdugo Road, Glendale, CA 91208-1665 (US).

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM,

AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: BISMUTH CONTAINING FLUOROPHOSPHATE GLASS AND METHOD FOR MAKING THEREOF

(57) Abstract: New and improved compositions of doped and co-doped bismuth fluorophosphate glasses for lasers is disclosed that have a high refractive index (nD) of approximately 1.6 and higher, high transmission in the near infrared part of the spectrum, and a wide glass forming domain. The disclosed glass systems A1(PO3)3- Ba(PO3)2- Bi(PO3)3- BaF2 + RFX + dopands use dopants from the group of oxides and or fluorides of rare earth elements Nd Er, Yb, Tm, Tb, Ho, Sm, Eu and Pr as we as MnO and mixtures thereof over 100 percent (wt%) of the glass-base composition. These glasses have high chemical durability, radiation resistance, efficiency of laser use in the infrared and blue spectrum, and improved duration of luminescence.



WO 2007/005953 A2

BISMUTH CONTAINING FLUOROPHOSPHATE GLASS AND METHOD FOR MAKING THEREOF

BACKGROUND OF THE INVENTION

5 (1) Field of the Invention

This invention relates to doped fluorophosphate optical grade glasses and, more particularly, to bismuth containing doped/co-doped fluorophosphate optical grade glasses.

10 (2) Description of Related Art

Most conventional optical grade glasses are manufactured on a SiO₂ base, and are appropriately doped to form silicate laser glasses. The optical grade SiO₂ doped glasses have a limited refractive index of about $n_D = 1.40$ to 1.45, which limit their infrared transmission spectrum, and have a high dispersion rate of approximately
15 45 to 50. These limitations prohibit the use of SiO₂ based optical glasses in the newer laser applications that require efficient transparency in the near and mid infrared frequency range. In general, the SiO₂ based glasses have a maximum infrared transmission of about 2.5 μm to 3.0 μm . A further limitation with SiO₂ based optical grade glasses is that they also have a low Gamma and Neutron radiation resistance.
20 The SiO₂ base optical grade glasses darken under Gamma and Neutron radiation due to their low Gamma radiation resistance - a process known as solarization, making them impractical for uses in the space and nuclear applications.

Other optical grade glass systems include the phosphate based glasses of
25 varying compositions, disclosed in U.S. Patents 3,846,142; 4,962,067; 6,430,349; and 4,771,020. However, these glasses contain alkaline elements. In general, glasses containing alkaline elements have low hardness, and low chemical durability or stability, none of which are suitable properties appropriate for use in newer laser applications.

30

Still other optical grade glass systems include fluorophosphate based glasses of varying compositions. In general, known fluorophosphate optical grade glasses have a refractive index of approximately $n_D = 1.55$ to 1.59 and a low dispersion of approximately 50 to 68. However, none provide the efficient transmission qualities in the near and mid infrared frequency range required for newer laser applications.

Existing fluorophosphate optical grade glasses such as the system $\text{BaPO}_3\text{F-MgF}_2\text{-Nd}_2\text{O}_3\text{-Ga}_2\text{O}_3\text{-MnO}$ have a high rate of inactive absorption of wavelength 1,064 nm, which reduces the luminescence of glass dopants. The inactive absorption may be defined as optical "noise." There are also a class of fluorophosphate laser glasses that were developed on a metaphosphate aluminum and fluorides of metals from the first and second group of the periodic elements (2,511,225; 2,511,227; 2,481,700; and 2,430,539). However, the refractive index for these glasses are in the range (n_D) from about 1.45 to 1.59, which are not very high.

U.S. Patent Nos. 6,429,162; 4,120,814; 4,771,020; and 5,755,998 disclosed various fluorophosphate optical grade glasses that include alkaline elements that inherently have limited chemical durability, laser performance, and reduced Gamma and Neutron radiation resistance, making their application in space and nuclear energy industries impractical.

The U.S. patent application 20030040421 to Margaryan disclosed a fluorophosphate glass system that is based on only two raw compounds used for glass formations, the metaphosphates of Barium $\text{Ba}(\text{PO}_3)_2$ and Aluminum $\text{Al}(\text{PO}_3)_3$. However, the use of only two raw compounds for glass formations limits the glass-forming domain (i.e., limiting the number of permutations for the glass formations (or types) that can be produced). In addition, the glass systems that are disclosed in the U.S. patent application 20030040421 have insufficient laser performance and Gamma and Neutron radiation resistance. The glass systems disclosed used single anti-radiation element barium (Ba), with an ytterbium element as a dopant that functions to create a constant process similar to di-solarization.

Other glass systems include those taught by the U.S. Patent 6,495,481 to Margaryan, the entire disclosure of which is incorporated herein by this reference. The U.S. Patent 6,495,481 to Margaryan disclosed germanium-fluorophosphate glass systems with network structure based on germanium dioxide. However, the germanium dioxide based network structures are not suitable for radiation resistance applications due to the presence of GeO₂.

There are several publications that discuss compositions of bismuth containing glasses. The publication titled "The Bismuth Atom Neighborhood in Bismuth Silicate Glasses From X-Ray Absorption Experiment," by Agnieszka Witkowska et al., 6th International Conference on Intermolecular Interaction In Matter, Gdansk- Poland, September 10 - 13, 2001 investigated the structure of bismuth containing silicate glasses using X-Ray absorption experiment.

The publication titled "Ultrafast Optical Switch and Wavelength Division Multiplexing (WDM) Amplifiers Based on Bismuth Oxide Glasses," by Naoki Sugimoto, Research Center, Asahi Glass Co., Ltd., Yokohama 221 - 8755, Vol. 85 No. 5, May 2002 Japan, disclosed a Bismuth Oxide based optical switching system. However, as with other SiO₂ based system, in general, these glasses cannot be used in space and nuclear energy industries due to their low Gamma and Neutron radiation resistance.

The publication titled "Spectroscopic properties of Mn²⁺ in new bismuth and lead contained fluorophosphates glasses," by A. Margaryan et al., published in Applied Physics, B78, 409-413 (2004) disclosed a glass system with no dopants (with the exception of Mn²⁺). The glasses taught in this publication could not be used for laser applications, nor can they be used in space and nuclear energy industries due to lack of dopants that improve radiation resistance in glass.

The publication titled "Erbium – doped potassium bismuth gallate glass," by Wong et al., Journal of the Optical Society of America, (Optical Physics), Volume 19, Issue 8, 1839- 1843, Aug 2002, disclosed potassium bismuth gallate glasses as suitable hosts for rare-earth-ion erbium (Er^{3+}) operating in the 1.55- μm wavelength region. However, due to the use of potassium, these glass systems have a very low chemical stability and durability, and in general, could not be used in space and nuclear energy industries due to their low Gamma and Neutron radiation resistance.

The publication titled "Emission properties of PbO - Bi_2O_3 - Ga_2O_3 - GeO_2 glasses doped with Tm^{3+} and Ho^{3+} ," by Jay Hyok Song et al., Journal of Applied Physics, June 15, 2003, Volume 83, Issue 12, pp. 9441-9445 disclosed the use of GeO_2 having low chemical durability within the disclosed glass system.

The publication titled "Physical Properties of Novel Lead Bismuthate Glasses with Large Transmitting Windows," by Sun Hong Tao et al., Shanghai Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, Shanghai 201800, 2004 Chinese Physics. Lett. 21 1759- 1761, disclosed a Pb based glass system, which impedes its use in space and nuclear energy industries, in particular, in a high Gamma and Neutron radiation environment.

Other materials such as optical crystals rather than optical glasses are also available. However, optical crystals (crystalline material in general) offer many disadvantages in terms of manufacture, yield (amount of raw material needed to produce the desired amount of crystalline product), and variation in optical characteristics, etc. For example, in general, the composition of glasses may easily be varied to produce different optical characteristics; this cannot be easily accomplished with crystals. Furthermore, crystal growth is slow, requires the applications of complex technologies, and is costly to produce.

In light of the current state of the art and the drawbacks to current devices, a need exists for a glass that would have a high refractive index, wider infrared

transmission spectrum, high thermal expansion, high hardness properties, high chemical durability or stability, low dispersion, high level of luminescence, and low rate of inactive absorption (low rate of optical noise) for a more efficient transparency in a wide frequency range from ultraviolet to infrared. In addition, in order to use the glass in space and nuclear energy industries a need exists for a glass that would also have a high Gamma and Neutron radiation resistance.

BRIEF SUMMARY OF THE INVENTION

The present invention provides bismuth fluorophosphate glass compositions, non-limiting exemplary uses of which may include laser applications, amplifiers, radiation resistant windows and fibers, high density optical storage, etc. Due to their unique spectroscopic properties, the bismuth fluorophosphate vitreous materials can be used for ultraviolet, visual, and near infrared optics in the exemplary band of about 250 to 3,500 nm.

The bismuth fluorophosphate glass of the present invention contains a combination of the components $\text{Al}(\text{PO}_3)_3$, $\text{Ba}(\text{PO}_3)_2$, and $\text{Bi}(\text{PO}_3)_3$, which constitute the glass formation of the present invention. The addition of BaF_2 to the glass formation comprises the glass-base of the present invention. An alternative glass-base may also be comprised of $\text{BaF}_2 + \text{RFX}$, where RFX is selected from the group consisting of preferably MgF_2 , CaF_2 , PbF_2 , and BiF_3 , or related fluorides to form the alternative glass-base of the present invention. In addition, optional dopants/co-dopants MnO and or M_2O_3 and or MF_3 , where M is selected from the group consisting of Nd , Er , Tm , Ho , Pr , Tb , Sm , Eu , and Yb over 100 wt. % of the glass-base may be used to compose an optical grade glass in accordance with the present invention.

In other words, a combination of the components $\text{Al}(\text{PO}_3)_3$, $\text{Ba}(\text{PO}_3)_2$, and $\text{Bi}(\text{PO}_3)_3$ constitute a ternate glass formation in accordance with the present invention. The addition of BaF_2 to the ternary glass formation constitutes the glass-base of the present invention ($\{\text{Glass Formation}\} + \{\text{BaF}_2\}$). Optionally, in addition

to BaF₂, RFX may also be added to the glass-base to form an alternative glass-base ({Glass Formation} + {BaF₂ + (optional) RFX}). The RFX is selected from the group consisting of preferably MgF₂, CaF₂, PbF₂, and BiF₃, or related fluorides. With the optional addition of dopants/co-dopants MnO and/or M₂O₃ and/or MF₃ over 100 wt. percent of the glass-base ({Glass Formation} + {BaF₂ + (optional) RFX}), the optical grade glass of the present invention is composed, with the M is selected from the group consisting of Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu, and Yb. The disclosed composition of the glasses of the present invention have a high level of chemical durability, laser efficiency, luminescence energy, Gamma and Neutron radiation resistance, and superior optical characteristics suitable for high density optical storage.

These and other features, aspects, and advantages of the invention will be apparent to those skilled in the art from the following detailed description of preferred non-limiting exemplary embodiments, taken together with the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

There are no drawings.

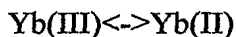
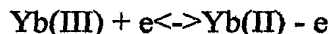
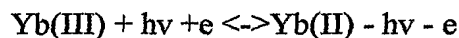
DETAILED DESCRIPTION OF THE INVENTION

The present invention provides glass compositions that are particularly useful in laser glass, amplifiers, radiation resistant windows and fibers, high density optical storage applications, and more. The glass composition of the present invention provide superior optical characteristics with a refractive index from about 1.63 to 1.65 and a dispersion from about 67 to 68. The non-silicate base glass of the present invention is also highly Gamma and Neutron radiation resistant. The new bismuth based fluorophosphate glasses have a better performance in Gamma radiation environment due to the unique characteristics of bismuth (Bi).

Generally, most of the fluorophosphate glasses are synthesized on the barium, aluminum, lead, calcium, strontium, zinc, magnesium, or sodium metaphosphate

bases. Creation of glasses that can perform in harsh Gamma radiation environment requires a proper selection of the right type of modifiers elements. Although fluorophosphate glasses containing barium (Ba) or lead (Pb) are excellent candidates for creation of radiation resistance vitreous material, due to the environmental issues it has been determined that lead (Pb) containing glasses may cause problems after they are exposed to high levels of Gamma radiation. In accordance with the present invention, the best and better replacement for lead (Pb) in radiation resistance glasses is bismuth (Bi).

In addition to bismuth (Bi), the glass system of the present invention further includes barium (Ba) and aluminum (Al). The presence of two antiradiation modifiers atoms (bismuth and barium) substantially increases the Gamma radiation resistance. To further enhance the performance, rare earth elements, a nonlimiting example of which is ytterbium (Yb) can be added as an optional dopant to the base compositions of the glass of the present invention. Ytterbium dopant increases the Gamma and Neutron radiation resistance and improves the optical characteristics of the glass systems of the present invention in terms of higher refractive index, high durability, and high visible transparency that is critical for making a glass fiber. The ytterbium dopant increases the radiation resistance of the glass of the present invention in accordance with the following chemical process or transformations at the exemplary wavelength of about (333nm):



where $h\nu$ is energy of the Gamma ray, and e is the electron. The super-fast transformation or oscillations of Yb valency from (III) to (II) and reverse creates a constant process similar to disolorization that allows the ternate glass matrix of the present invention to stay transparent during Gamma radiation. Nonlimiting examples of other rare earth elements in small amounts (e.g., 0.02 to 0.05 mol %) that withstood high levels of irradiation include Samarium ($\text{Sm(III)} \leftrightarrow \text{Sm(II)}$) at the exemplary

wavelength range of about 280 - 360nm) and Europium (Eu(III) \leftrightarrow Eu(II) at the exemplary wavelength of about 310 nm).

5 The bismuth containing fluorophosphate glass of the present invention can be classified with a "CR1" class rating for high chemical durability. The chemical durability (or climatic resistance) classification "CR1" of the composition of the present invention is based on the Schott Glass classification scheme. The Schott Glass categorizes climatic resistances of various glasses (their chemical durability) into four classes from CR1 to CR4, with CR1 representing a high climatic resistance for a glass 10 when exposed to 100% relative humidity in air, thermally cycled between 45 °C to 55 °C each hour. The chemical durability for the bismuth fluorophosphate glass of the present invention meets the requirements of the Schott Glass CR1 classification scheme. This classification scheme is published in Optical Engineering, Volume 6, pages 40 - 45, titled "Optical Materials An Introduction to Selection and Application," 15 1985, by Solomon Musikan.

Fluorophosphate based glasses are close to the phosphate glasses in terms of the degree of covalence of the dopant- ligand bond. This has been confirmed by comparison of the Racha coefficient, B , for these glasses. The magnitude of B 20 decreases with a decrease in size of the effective nuclear charge of free ions. The boundary of glass formation and glass-base for fluorophosphate glasses with metaphosphate of barium, metaphosphate of bismuth, metaphosphate of aluminum and with fluorides of earth alkaline elements create a wide domain of glass forming fluorophosphate that increase in the following order $Ba > Sr > Ca > Mg$. The 25 presence of barium fluoride, BaF_2 , with the added optional RF_x , where RF_x is selected from the group consisting of MgF_2 , CaF_2 , PbF_2 , and BiF_3 effectively increases and improves chemical durability, Gamma radiation resistance, and laser characteristics

30 The bismuth fluorophosphate glass of the present invention contains a combination of the components $Al(PO_3)_3$, $Ba(PO_3)_2$, and $Bi(PO_3)_3$, which constitute

the glass formation of the present invention. The addition of BaF₂ to the glass formation comprises the glass-base of the present invention. An alternative glass-base may also be comprised of BaF₂ + RF_x, where RF_x is selected from the group consisting of preferably MgF₂, CaF₂, PbF₂, and BiF₃, or related fluorides to form the alternative glass-base of the present invention. In addition, optional dopants/co-dopants MnO and or M₂O₃ and or MF₃, where M is selected from the group consisting of Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu, and Yb over 100 wt. % of the glass-base may be used to compose an optical grade glass in accordance with the present invention.

In other words, a combination of the components Al(PO₃)₃, Ba(PO₃)₂, and Bi(PO₃)₃ constitute a ternary glass formation in accordance with the present invention. That is, ternary raw compounds used for the glass formation of the present invention are Metaphosphates of Aluminum Al(PO₃)₃, Barium Ba(PO₃)₂, and Bismuth, Bi(PO₃)₃, which are considered chemically stable substances. The use of three raw compounds for glass formations increases the glass-forming domain (i.e., the number of permutations for the glass formations (or types) that can be produced). The addition of BaF₂ to the ternary glass formation constitutes the glass-base of the present invention ({Glass Formation} + {BaF₂}). Optionally, in addition to BaF₂, RF_x may also be added to the glass-base to form an alternative glass-base ({Glass Formation} + {BaF₂ + (optional) RF_x}). The RF_x is selected from the group consisting of preferably MgF₂, CaF₂, PbF₂, and BiF₃, or related fluorides. With the optional addition of dopants/co-dopants MnO and/or M₂O₃ and/or MF₃ over 100 wt. percent of the glass-base ({Glass Formation} + {BaF₂ + (optional) RF_x}), the optical grade glass of the present invention is composed, with the M is selected from the group consisting of Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu, and Yb. The disclosed composition of the glasses of the present invention have a high level of chemical durability, high laser efficiency, high luminescence energy, high gamma radiation resistance, and superior optical characteristics suitable for high density optical storage.

Table I below details twenty-one (21) exemplary sample ranges for the composition of the ternary glass formation components {Bi(PO₃)₃, Al(PO₃)₃, and Ba(PO₃)₂} and the combining of the fluorides {BaF₂ + (optional) R_Fx} with the glass formations to form the glass-base (1),

5

{Bi(PO₃)₃, Al(PO₃)₃, and Ba(PO₃)₂} + {BaF₂ + (optional) R_Fx} = 100 Mol %, (1)

plus the optional addition of dopants / codopants (2) to form the bismuth fluorophosphate glass of the present invention,

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{Glass-Base }(100 Mol %) + {Optional Dopants/Co-dopants} (wt %). (2)

TABLE I

{Bi(PO ₃) ₃ , Al(PO ₃) ₃ , and Ba(PO ₃) ₂ } in Mol %: (Glass Formations)			+ {BaF ₂ + (optional) RfX} in Mol %: (Glass-Base)			+ {Optional Dopants / Co- dopants MnO and/or M ₂ O ₃ and/or MF ₃ over 100 wt percent of Glass-Base}		
Preferred	Most Preferred	Especially Preferred	Preferred	Most Preferred	Especially Preferred	Preferred	Most Preferred	Especially Preferred
Bi (PO ₃) ₃ 16-94	Bi (PO ₃) ₃ 19-80	Bi (PO ₃) ₃ 9-14						
Al (PO ₃) ₃ 4.5-5	Al (PO ₃) ₃ 1-5	Al (PO ₃) ₃ 1-5	0.5-79	10-79	65-79	0.1-20	2-7	2.5
Ba (PO ₃) ₂ 0.5-0.5	Ba (PO ₃) ₂ 1-5	Ba (PO ₃) ₂ 11-16						
Bi (PO ₃) ₃ 0.5-78	Bi (PO ₃) ₃ 4.5-47	Bi (PO ₃) ₃ 5-10						
Al (PO ₃) ₃ 10.5-11	Al (PO ₃) ₃ 16-35	Al (PO ₃) ₃ 5-10	0.5-79	13-79	64-79	0.1-20	6-15	1.5
Ba (PO ₃) ₂ 10-10.5	Ba (PO ₃) ₂ 0.5-5	Ba (PO ₃) ₂ 11-16						
Bi (PO ₃) ₃ 7-35	Bi (PO ₃) ₃ 5-30	Bi (PO ₃) ₃ 9-14						
Al (PO ₃) ₃ 7-35	Al (PO ₃) ₃ 10-40	Al (PO ₃) ₃ 6-11	0.5-79	1-79	64-79	0.1-20	1-3	5
Ba (PO ₃) ₂ 7-29.5	Ba (PO ₃) ₂ 6-29	Ba (PO ₃) ₂ 6-11						
Bi (PO ₃) ₃ 4-5	Bi (PO ₃) ₃ 1-15	Bi (PO ₃) ₃ 6-11						
Al (PO ₃) ₃ 16.5-94	Al (PO ₃) ₃ 15-50	Al (PO ₃) ₃ 10-15	0.5-79	10-66	63-79	0.1-20	6-15	7.5
Ba (PO ₃) ₂ 0.5-0.5	Ba (PO ₃) ₂ 18-25	Ba (PO ₃) ₂ 5-11						
Bi (PO ₃) ₃ 10.5-11	Bi (PO ₃) ₃ 5-10	Bi (PO ₃) ₃ 8-13						
Al (PO ₃) ₃ 0.5-78	Al (PO ₃) ₃ 7-40	Al (PO ₃) ₃ 5-10	0.5-79	5-79	64-79	0.1-20	1-10	1-3.5
Ba (PO ₃) ₂ 10-10.5	Ba (PO ₃) ₂ 9-45	Ba (PO ₃) ₂ 8-13						
Bi (PO ₃) ₃ 10-10.5	Bi (PO ₃) ₃ 5-10	Bi (PO ₃) ₃ 1-5						
Al (PO ₃) ₃ 10.5-11	Al (PO ₃) ₃ 15-60	Al (PO ₃) ₃ 9-14	0.5-79	20-65	65-79	0.1-20	4-6	3
Ba (PO ₃) ₂ 0.5-78	Ba (PO ₃) ₂ 5-10	Ba (PO ₃) ₂ 11-16						
Bi (PO ₃) ₃ 4.5-5	Bi (PO ₃) ₃ 12-16	Bi (PO ₃) ₃ 15-16						
Al (PO ₃) ₃ 0.5-0.5	Al (PO ₃) ₃ 15-40	Al (PO ₃) ₃ 5-10	0.5-79	14-70	58-79	0.1-20	3-8	1.5
Ba (PO ₃) ₂ 16-94	Ba (PO ₃) ₂ 3-30	Ba (PO ₃) ₂ 1-16						

In particular, an exemplary, nonlimiting, especially preferred material for the present invention are glasses containing $\text{Al}(\text{PO}_3)_3$ of about 5 to 10 mol %, $\text{Ba}(\text{PO}_3)_2$ of about 8 to 13 mol %, and $\text{Bi}(\text{PO}_3)_3$ of about 8 to 13 mol %, which constitute a ternary glass formation of the present invention. The addition of BaF_2 + (optional) R_Fx of about 64 to 79 mol % compose the base material (the glass-base), where the optional R_Fx is selected from the group consisting of MgF_2 , CaF_2 , PbF_2 , and BiF_3 . The addition of the optional dopants/codopants over 100 wt. % of the glass-base such as MnO and or M_2O_3 and or MF_3 of about 1 to 3.5 weight %, where M is selected from the group consisting of Nd, Er, Tm, Ho, Pr, Tb, Sm, Eu and Yb, will comprise the optical grade glass of the present invention.

For the glass compositions of the present invention, the duration of luminescence for neodymium ions in the laser wavelength of about 1064 nm is approximately 430 to 460 msec and the half width of luminescence is approximately 160 to 165 cm^{-1} . For erbium ions, the duration of luminescence for the glass composition of the present invention in the laser wavelength of about 1535 nm is approximately 490 to 510 msec and the half width of luminescence is approximately 150 to 155 cm^{-1} . The emission cross section for ytterbium was found to be about 0.87 pm^2 at the lasing wavelength of about 996 nm. This is a very high level among fluorophosphate laser glasses. Most conventional fluorophosphate laser glasses have an emission cross section of about 0.68 pm^2 at the same wavelength of 996 nm. The glass composition of the present invention also exhibits an extremely high gain coefficient of about 0.95 $\text{ms}\cdot\text{pm}^4$, and high quantum efficiency of about 94%. The combination of spectroscopic (high emission cross section and gain coefficient) and optical (low dispersion and small nonlinear refractive index) properties demonstrates that the glass compositions of the present invention, such as the current ytterbium activated bismuth fluorophosphate glass is an excellent candidate for fiber and waveguide lasers.

A neodymium, erbium, and ytterbium doped athermal bismuth fluorophosphate glass results from the high neodymium, erbium, and ytterbium

oxide or fluoride concentration of about 4 to 6 weight %. Erbium doped bismuth fluorophosphate laser glass requires less excitation energy to emit light at the appropriate wavelength and therefore, more efficient than Erbium doped silicate glasses. In other words, the amount of energy required to excite the Erbium doped bismuth fluorophosphate glass is less than the energy needed to excite erbium doped silicate laser glass. Erbium doped bismuth fluorophosphate laser glass also has an eye safe operating wavelength of about 1535 nm, which makes it useful for specialized medical apparatus. The combination of the glass-base and dopands of the present invention provide an efficient laser glass in the infrared and blue region for laser use.

The preferred glass forming compounds of the present invention $\text{Al}(\text{PO}_3)_3$, $\text{Ba}(\text{PO}_3)_2$, and $\text{Bi}(\text{PO}_3)_3$ are characterized as chemically stable substances. When combined, they create a significant free and open volume structure due to the large ionic radii of barium and bismuth. The nonlimiting examples of barium and bismuth containing glass formations may include $\text{Ba}(\text{PO}_3)_2$ and $\text{Bi}(\text{PO}_3)_3$. The addition of BaF_2 + (optional) RF_x (e.g., BiF_3) will constitute the glass-base and provide the additional advantage of a free and open volume structure for the glass composition of the present invention. This added free space allows the homogenous and regular distribution of dopant / codopant ions in the glass matrices, improving optical characteristics. In other words, the larger free volume provides a greater freedom for dopants / codopants to excite (more room to vibrate) when energized.

The presence of BaF_2 + RF_x effectively increases the chemical durability of the optical material. As described above, in the grouping of glasses according to chemical stability of non-silicate glasses relating to humidity or moisture, the glasses of the present invention are considered to be stable. During the melting process a chemical integration between $\text{Ba}(\text{PO}_3)_2$ and BaF_2 creates BaPO_3F , monofluorophosphate barium. The melting process is conducted in the temperature range of about 1150 °C to 1350 °C in vitreous carbon crucibles in a dry argon atmosphere for about 4 to 6 hours followed by an annealing temperature range of about 300 °C to 360 °C for about 8 to 15 hours. In the system of $\text{Al}(\text{PO}_3)_3$ -

Ba(PO₃)₂- Bi(PO₃)₃- BaF₂- RF_x two separate glass forming ranges were discovered, both of which are illustrated in Table II.

TABLE II

	Glass Formations		Glass-Base
	Ba(PO ₃) ₂ + Al(PO ₃) ₃	Bi(PO ₃) ₃	BaF ₂ + RF _x
RANGE - I (in mol %)	7 - 45	14 - 50	5 - 79
RANGE - II (in mol %)	16 - 45	5 - 10	45 - 79

- 5 Examples of effective compositions and properties of the bismuth fluorophosphate laser glass for the composition Al(PO₃)₃-Ba(PO₃)₂- Bi(PO₃)₃- BaF₂-RF_x- Nd₂O₃ or Er₂O₃ are illustrated in Table III based on mol percent and dopands over 100 wt % of the glass-base.

TABLE III

Composition of Glass (mol %)			Dopant (wt %)		Refractive	Density	Quantum
Ba(PO ₃) ₂ + Al(PO ₃) ₃	Bi(PO ₃) ₃	BaF ₂ + RF _x	Nd ₂ O ₃	Er ₂ O ₃	Index (nD)	(g/cm ³)	Yield (%) luminescence
42	48	10	2	-	1.6434	3.38	47
35	15	50	2	-	1.6485	3.41	63
30	10	60	2	-	1.6501	3.45	67
10	20	70	2	-	1.6445	3.48	73
40	50	10	-	2	1.6386	3.38	55
35	15	50	-	2	1.6406	3.40	64
28	12	60	-	2	1.6485	3.48	70
10	20	70	-	2	1.6440	3.45	77

10

In the above table III example, MnO and Yb₂O₃ may be used as co-dopants.

While the invention has been described in detail and with reference to specific embodiments thereof, it will be apparent by those skilled in the art that various

changes and modifications can be made therein without departing from the spirit and scope thereof.

CLAIMS

What is claimed is:

1. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:
 - 5 a metaphosphate $\text{Al}(\text{PO}_3)_3$, from 5 to 10 percent;
 - a metaphosphate $\text{Ba}(\text{PO}_3)_2$, from 8 to 13 percent;
 - a metaphosphate $\text{Bi}(\text{PO}_3)_3$, from 8 to 13 percent;
 - fluorides $\text{BaF}_2 + \text{RF}_x$, from 64 to 79 percent; and
 - a rare earth dopant M_2O_3 or MF_3 over 100 wt %;
- 10 where

R is selected from the group consisting of Ca, Mg, Pb, and Bi;

x is an index representing an amount of fluoride (F) in the compound RF_x ; and

M is selected from the group consisting of Lanthanide series.
- 15 2. The bismuth fluorophosphate glass as set forth in claim 1, wherein the rare earth dopant M_2O_3 or MF_3 over 100 wt %, are at 0.5 to 20 wt percent, with M selected from the group consisting of:
 - neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb),
 - holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide
 - 20 of manganese (Mn); and mixtures thereof.
3. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:
 - 25 a metaphosphate $\text{Al}(\text{PO}_3)_3$, from 4.5 to 5 percent;
 - a metaphosphate $\text{Ba}(\text{PO}_3)_2$, from 0.5 to 0.5 percent;
 - a metaphosphate $\text{Bi}(\text{PO}_3)_3$, from 16 to 94 percent;
 - fluorides $\text{BaF}_2 + \text{RF}_x$, from .5 to 79 percent; and
 - a dopant over 100 wt% comprised of M_2O_3 or MF_3 at 0.5 to 20 wt percent,
 - with M selected from a group consisting of rare earth elements:

neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide of manganese (Mn); and mixtures thereof;

where

- 5 R is selected from the group consisting of Ca, Mg, Pb, and Bi; and
 x is an index representing an amount of fluoride (F) in the compound RF_x .

4. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:

- 10 a metaphosphate $\text{Al}(\text{PO}_3)_3$, from 10.5 to 11 percent;
 a metaphosphate $\text{Ba}(\text{PO}_3)_2$, from 10 to 10.5 percent;
 a metaphosphate $\text{Bi}(\text{PO}_3)_3$, from 0.5 to 78 percent;
 fluorides $\text{BaF}_2 + \text{RF}_x$, from 0.5 to 79 percent; and
 dopant over 100 wt% comprised of M_2O_3 or MF_3 at 0.5 to 20 percent, with M
15 selected from a group consisting of rare earth elements:

neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide of manganese (Mn); and mixtures thereof;

where

- 20 R is selected from the group consisting of Ca, Mg, Pb, and Bi; and
 x is an index representing an amount of fluoride (F) in the compound RF_x .

5. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:

- 25 a metaphosphate $\text{Al}(\text{PO}_3)_3$, approximately 10.5 to 11 percent;
 a metaphosphate $\text{Ba}(\text{PO}_3)_2$, approximately 0.5 to 78 percent;
 a metaphosphate $\text{Bi}(\text{PO}_3)_3$, approximately 10 to 10.5 percent;
 fluorides $\text{BaF}_2 + \text{RF}_x$, approximately 0.5 to 79 percent; and
 dopant over 100%, comprised of approximately 2 to 5 wt percent of oxide of
30 neodymium (Nd);
 where R is selected from the group consisting of Ca, Mg, Pb, and Bi; and

x is an index representing an amount of fluoride (F) in the compound RF_x .

6. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:

5 a metaphosphate $\text{Al}(\text{PO}_3)_3$, approximately 0.5 to 0.5 percent;
 a metaphosphate $\text{Ba}(\text{PO}_3)_2$, approximately 16 to 94 percent;
 a metaphosphate $\text{Bi}(\text{PO}_3)_3$, approximately 4.5 to 5 percent;
 fluorides $\text{BaF}_2 + \text{RF}_x$, approximately 0.5 to 79 percent; and
 dopant over 100%, comprised of approximately 2 to 5 wt percent of oxide of
 10 erbium (Er);
 where R is selected from the group consisting of Ca, Mg, Pb, and Bi; and
 x is an index representing an amount of fluoride (F) in the compound RF_x .

7. A method for making a bismuth fluorophosphate glass, comprising the acts of:

15 batching glass components;
 melting glass components to form a molten mixture;
 cooling the molten mixture to solid state;
 annealing glass in the solid state;
 slowly cooling the annealing glass to approximately ambient temperature;
 20 the glass components, on a mol basis, comprising of:
 a metaphosphate $\text{Al}(\text{PO}_3)_3$, from 5 to 10 percent;
 a metaphosphate $\text{Ba}(\text{PO}_3)_2$, from 8 to 13 percent;
 a metaphosphate $\text{Bi}(\text{PO}_3)_3$, from 8 to 13 percent;
 fluorides $\text{BaF}_2 + \text{RF}_x$, from 64 to 79 percent; and
 25 dopant over 100 wt% comprised of M_2O_3 or MF_3 at 0.5 to 20 wt percent,
 with M selected from a group consisting of rare earth elements:
 neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium
 (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium
 (Pr); an oxide of manganese (Mn); and mixtures thereof;
 30 where
 R is selected from the group consisting of Ca, Mg, Pb, and Bi; and

x is an index representing an amount of fluoride (F) in the compound RF_x .

8. The method as set forth in claim 7, wherein the melting of the glass is in a temperature range of 1150 °C to 1350 °C in vitreous carbon crucibles in a dry Argon atmosphere for 4 to 6 hours.

9. The method as set forth in claim 7, wherein the annealing of the glass is in the temperature range of 300 °C to 360 °C for approximately 8 to 15 hours.

10. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:

a metaphosphate $\text{Al}(\text{PO}_3)_3$, approximately 0.5 to 78 percent;
a metaphosphate $\text{Ba}(\text{PO}_3)_2$, approximately 10 to 10.5 percent;
a metaphosphate $\text{Bi}(\text{PO}_3)_3$, approximately 10.5 to 11 percent;
fluorides $\text{BaF}_2 + \text{RF}_x$ approximately 0.5 to 79 percent; and
a dopant over 100%, approximately 0.5 to 5 wt percent comprised of M_2O_3 or MF_3 , with M selected from a group consisting of rare earth elements:

neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide of manganese (Mn); and mixtures thereof;

where R is selected from the group consisting of Ca, Mg, Pb, and Bi;

x is an index representing an amount of fluoride (F) in the compound RF_x , forming fluorides selected from the group consisting of CaF_2 , MgF_2 , PbF_2 , and BiF_3 .

11. A bismuth fluorophosphate glass formed from a composition comprising on a mol basis:

a metaphosphate $\text{Al}(\text{PO}_3)_3$, approximately 16.5 to 94 percent;
a metaphosphate $\text{Ba}(\text{PO}_3)_2$, approximately 0.5 to 0.5 percent;
a metaphosphate $\text{Bi}(\text{PO}_3)_3$, approximately 4 to 5 percent;
fluorides $\text{BaF}_2 + \text{RF}_x$, approximately 0.5 to 79 percent; and

a dopant over 100%, approximately 0.5 to 10 wt percent of M_2O_3 or MF_3 , with M selected from a group consisting of rare earth elements:

neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide of manganese (Mn); and mixtures thereof;

where R is selected from the group consisting of Ca, Mg, Pb, and Bi;

x is an index representing an amount of fluoride (F) in the compound RF_x , forming fluorides selected from the group consisting of CaF_2 , MgF_2 , PbF_2 , and BiF_3 .

12. A method for making a bismuth fluorophosphate glass comprising the acts of:
batching glass components;

melting glass components to form a molten mixture;

cooling the molten mixture to solid state;

annealing the glass in the solid state;

slowly cooling the annealing glass to approximately ambient temperature;

the glass components, on a mol basis, comprising of:

a metaphosphate $Al(PO_3)_3$, from 5 to 10 percent;

a metaphosphate $Ba(PO_3)_2$, from 11 to 16 percent;

a metaphosphate $Bi(PO_3)_3$, from 5 to 10 percent;

fluorides $BaF_2 + RF_x$, from 64 to 79 percent; and

dopant over 100 wt% comprised of M_2O_3 or MF_3 at 0.5 to 20 percent, with M selected from a group consisting of rare earth elements:

neodymium (Nd), erbium (Er), ytterbium (Yb), thulium (Tm), terbium (Tb), holmium (Ho), samarium (Sm), europium (Eu), praseodymium (Pr); an oxide of manganese (Mn); and mixtures thereof;

where

R is selected from the group consisting of Ca, Mg, Pb, and Bi; and

x is an index representing an amount of fluoride (F) in the compound RF_x .

13. The method as set forth in claim 12, wherein the melting of the glass is in temperature range of 1150 °C to 1350 °C in vitreous carbon crucibles in a dry Argon atmosphere for from 4 to 6 hours.
- 5 14. The method as set forth in claim 12, wherein the annealing of the glass is in the temperature range of 300 °C to 360 °C for from 8 to 15 hours.

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(57) Abstract: New and improved compositions of doped and co-doped bismuth fluorophosphate glasses for lasers is disclosed that have a high refractive index (nD) of approximately 1.6 and higher, high transmission in the near infrared part of the spectrum, and a wide glass forming domain. The disclosed glass systems $A_1(PO_3)_3$ - $Ba(PO_3)_2$ - $Bi(PO_3)_3$ - BaF_2 + RF_x + dopands use dopants from the group of oxides and or fluorides of rare earth elements Nd Er, Yb, Tm, Tb, Ho, Sm, Eu and Pr as well as MnO and mixtures thereof over 100 percent (wt%) of the glass-base composition. These glasses have high chemical durability, radiation resistance, efficiency of laser use in the infrared and blue spectrum, and improved duration of luminescence.



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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

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USPC - 501/44, 501/45, 65/117

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

USPC 501/44,45; 65/27,29,117

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Yahoo internet search, Google internet search, DialogPro (engineering) search

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST text search (glass, phosphate, metaphosphate, fluophosphate, fluorophosphate, po3, aluminum, barium, bismuth)

Yahoo 1 - 10 of about 76 for phosphate glass bismuth metaphosphate Barium aluminum

Google 1-10 of 65 for (phosphate, barium, aluminum, bismuth) and DialogPro 1 of 1 (phosphate, aluminum, barium, glass)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5,858,465 A (HUNT et al.) 12 January 1999 (12.01.1999), abstract	1-14
A	US 3,281,254 A (WEIDEL) 25 October 1966 (25.10.1966), column 2 line 47 to column 3 line 20	1-14
A	US 4,859,635 A (MEINERT et al.) 22 August 1989 (22.08.1989), abstract	1-14
A	US 6,495,481 B1 (MARGARYAN) 17 December 2002 (17.12.2002), abstract, columns 1-4	1-14
A	FLUOROPHOSPHATE VITREOUS SYSTEMS (MARGARYAN) 1999 http://web.archive.org/web/20050312075817/http://www.aforesearch.com/fpvs.html - web archive dated 12 March 2005 (12.03.2005), entire document	1-14

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